Mixing and Segregation in Binary Clusters(4) Quantum chaos and semiclassical theory in molecular science and nuclear theory, Chaos and Nonlinear Dynamics in Quantum-Mechanical and Macroscopic Systems)

AUTHOR(S):

YAMAMOTO, Norifumi; TAKATSUKA, Kazuo

Mixing and Segregation in Binary Clusters

Norifumi YAMAMOTO and Kazuo TAKATSUKA
Graduate School of Arts and Sciences, The University of Tokyo

要旨

二成分混合クラスターの偏析現象について報告する. Morse 型ポテンシャルを持つ 26 原子クラスター ($A_{13}B_{13}$) の時間発展過程について, 等エネルギー分子動力学計算を行なった. その結果, この種の原子クラスターにおいても, 粉粒体などで観測される大きさの違いによる偏析 (segregation by size) と同様, 原子間相互作用の違いによる偏析 (segregation by interaction) が, 一方向的に進行することを明らかにした.

1 Introduction

Mixing and segregation in binary systems are very familiar phenomena appearing in every field of physics. Recently experimental studies of mixing and segregation phenomena in binary molecular clusters have developed and its achievements have become a center of attraction. For example, Yasuda and Mori reported the behavior of spontaneous alloying process in bimetallic systems such as Au/Zn and Au/Cu nanoclusters by using the transmission electron microscopy (TEM) technique [1]. On the other hand, the self-assembling process of cluster formation which leads to radial segregation and layering has been observed in binary Ar/Xe clusters in an adiabatic expansion by Tchaplyguine et al. by using photoelectron spectroscopy measurements [2]. In this work we have studied how morphologies and features of the mixing and segregation dynamics in binary clusters depend on system parameters such as energies and potential parameters. We report here the results from the last investigation of various fundamental properties of the dynamics in binary clusters.

[1] H. Yasuda and H. Mori, *Phys. Rev. Lett.*, **69**, 3747 (1992).
[2] M. Tchaplyguine et al., *Phys. Rev. A*, **69**, 031201 (2004).

2 Model

The isoenergetic molecular dynamics (MD) calculations were performed to simulate N-atoms molecular clusters. The Hamiltonian we use is given by

$$H(\mathbf{q},\mathbf{p}) = \sum_{i}^{N} \frac{\mathbf{p}_i^2}{2m_{\sigma_i}} + \sum_{ij}^{N} V(r_{ij}) \qquad (1)$$

where $V(r_{ij})$ is the pairwise potential function depended on the interatomic distances r_{ij} between i-th and j-th atoms ($r_{ij} = |\mathbf{q}_i - \mathbf{q}_j|$). The model potential we adopt here is the Morse-type function written as

$$V = \sum_{ij}^{N} \epsilon_{\sigma_i\sigma_j} e^{r_{ij} - r_{\sigma_i\sigma_j}} \{ e^{r_{ij} - r_{\sigma_i\sigma_j}} - 2 \} \qquad (2)$$

where $r_{\sigma_i\sigma_j}$ and $\epsilon_{\sigma_i\sigma_j}$ are the equilibrium distance and potential depth determined by the species of interacting i-th and j-th atoms (σ_i and σ_j). In this study we focused on the dynamics of clusters which composed of two species labeled A and B. To simplify a parameter space we suppose that distances $r_{\sigma_i\sigma_j}$ are the same for two species, i.e., $r_{AA} = r_{BB} = r_{AB} \equiv \rho_0$. We further assume that $\epsilon_{AA} = \epsilon_{BB} \equiv \epsilon_0$. To correspond a topography of the model potential to that of the Lennard-Jones one we set the fixed parameters to $\rho_0 = 6.0$ and $\epsilon_0 = 1.0$. The only variable parameter of the model potential is defined as $\eta = (\epsilon_{AA} + \epsilon_{BB})/2 - \epsilon_{AB} = \epsilon_0 - \epsilon_{AB}$. In this report we present our studies about the segregation process in 26-atoms binary clusters, $A_{13}B_{13}$, setting the potential parameter to $\eta = 0.5$.

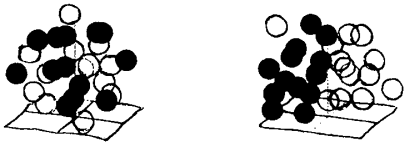

Figure 1: Mixing and Segregation

3 Results

To quantify the time dependence of the segregation process in binary clusters, we introduce the following parameter

$$\phi(t) = \frac{1}{N}\sum_{i}^{N} \frac{n_i^{hetero}(t)}{n_i^{homo}(t) + n_i^{hetero}(t)} \qquad (3)$$

where n_i^{homo} and n_i^{hetero} are the nearest neighboring *homo*geneous and *hetero*geneous atoms around the i-th atom at time t. Figure 2 shows the time dependence of mixing indexes, $\phi(t)$, obtained by the isoenergetic MD calculations. The initial energies of our calculations were selected in a range of E_1 (= -56.0) to E_4 (= -59.0), in which clusters are liquidlike and the particle evaporation is a rare event.

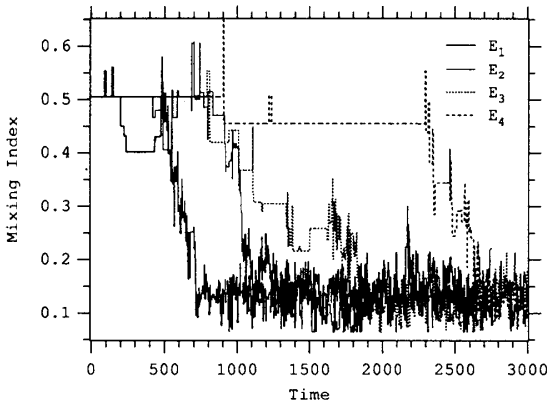

Figure 2: Time Evolution

In Fig.2, the mixing indexes $\phi(t)$ show directional evolutions from the mixing ($\phi \approx 0.5$) to demixing states and approaches to $\phi \approx 0.1$. Each index $\phi(t)$ evolves through a series of *plateau* and *growth* periods. Under the different initial energy the behavior of $\phi(t)$ has a different aspect in its time dependence. At the high energy simulations, the indexes show exponential increases and indicate smooth segregation of components in binary clusters. On the other hand, at the low energy simulations, the plateau parts in the lapse of the mixing index $\phi(t)$ persist for a longer time than those of the higher energy calculations. Furthermore, in these lower energy conditions, we found that even if at the very similar mixing index the duration of the plateau region are completely arbitrary for every trajectory. To quantify fluctuating and rearranging properties of atoms in clusters, we measured the Lindemann index, as followed:

$$\delta(t) = \frac{2}{N(N-1)}\sum_{i<j} \frac{\sqrt{\langle r_{ij}^2\rangle_t - \langle r_{ij}\rangle_t^2}}{\langle r_{ij}\rangle_t} \qquad (4)$$

where $\langle\cdots\rangle_t$ indicate the time average of the arbitrary quantity from t to $t+\Delta t$. In the early stage of $\phi(t)$ the Lindemann index is smaller than 0.1, which indicates that clusters are solidlike. From the time dependence of δ it is clear that as the mixing index decrease the Lindemann index rise rapidly. In the case of $\eta > 0$, the decay of $\phi(t)$ cause the generation of the heat of solution ΔH, which described by using the mixing index as $\Delta H \propto (1-\phi)\eta$. As the heat of solution ΔH increase the fluctuating motions of atoms accelerate and cause rearrangement reactions frequently. After the segregation the Lindemann index δ is large than 0.1 and indicates clusters are liquidlike. It is considered that the segregation process occur with the solid-liquid phase transition. Finally, to characterize the growth of $\phi(t)$, we perform the coarse graining of neglecting the plateau part in the time evolution. Counting the rearrangement reactions in clusters as one 'step', we investigate the conditions of mixing over the change of each step.

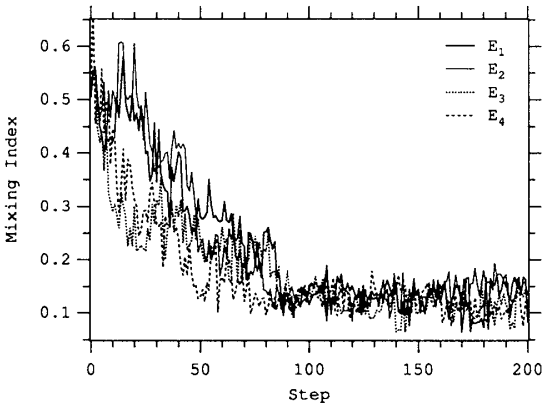

Figure 3: Step Evolution

The step evolutions $\phi(s)$ in Fig. 3 show the exponential decay of the mixing indexes, i.e., $\phi(s) \propto e^{-\tau s}$. Consequently, we extracted the fairly simple feature of the step-dependent dynamics successfully (in Fig. 3) from the complicated behavior of the time-dependent dynamics (in Fig. 2). Now we are attempting to clarify the origin and significance of them. Last, one of the authors (N.Y.) thanks to financial support from the JSPS research fellowships for young scientists.